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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Filler for Heat-Conductive Thermosetting Resins

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FM/6-18531/AFiller for heat-conductive thermosetting resinsAbstract of the Disclosure

A powder mixture of alumina with fractions of different particle size and external shape, which mixture comprises:

- (1) 55 to 75 % by volume of spherical α -alumina, at least 90 % by weight of which has an average particle size of 20 to 120 μm ,
 - (2) 35 to 20 % by volume of spherical alumina, at least 90 % by weight of which has an average particle size of 3 to 25 μm , and
 - (3) 10 to 1 % by volume of alumina, at least 90 % by weight of which has a particle size of 1 to 7 μm ,
- the percentages by volume adding up to 100 %.

The mixture is suitable for use as filler for synthetic resins, especially for casting resins, from which shaped articles of high thermal conductivity can be produced.

FM/6-18531/AFiller for heat-conductive plastics materials

The present invention relates to a formulation comprising three different fractions of alumina particles each having different particle diameters, which composition is suitable as filler for the production of heat-conductive plastics materials, to a formulation comprising a plastics material and said filler, and to the use of said formulation as moulding material for the production of moulded parts and composites.

Plastics materials are known to have poor thermal conductivity. To enhance their thermal conductivity therefore, finely particulate metallic or mineral fillers are blended into plastics materials. It is, however, only possible to use metallic fillers if no electrical insulating properties are required. Frequently used mineral fillers are quartz and silica, with which a thermal conductivity of up to about 2.5 W/mK is achieved with at high volume loadings or, preferably, alumina, with which it is possible to achieve a thermal conductivity of up to about 3.5 W/m. To avoid abrasion in moulds it is expedient to use spherical particles. It is also known that abrasion can be reduced by choosing particles of small size; but this also results in a reduction of volume loading and thus of thermal conductivity.

CA 112: 57551r (1990) discloses thermally conductive polymers which contain electrically fused alumina powder as filler. This filler is known to be abrasive, thereby limiting its utilities.

CA112:57894e (1990) discloses epoxy resins containing α -alumina as filler having an average particle diameter of 5 to 60 μm . The volume loading and thermal conductivity are considered inadequate.

CA 111: 175480u (1989) discloses thermally conductive polymers which contain a mixture of alumina and mainly spherical corundum having a very small particle diameter from 5 to 10 μm . High volume loadings and hence high thermal conductivities cannot be achieved with this filler.

It has now been found that it is possible to increase the volume loading further as well as to achieve higher thermal conductivities, such that the thermal coefficients of expansion are close to those of metals such as copper, silver or gold, by using as filler a mixture of alumina fractions of different particle size and different shape. It has also been found that this filler makes it possible to obtain low viscosity casting resins which have a very high filler loading and excellent castability and hence processibility.

In one of its aspects, the invention accordingly relates to a powdered mixture of alumina with fractions of different particle size and external shape, which mixture comprises:

- (1) 55 to 75 % by volume of spherical α -alumina, at least 90 % by weight of which has an average particle size of 20 to 120 μm ,
 - (2) 35 to 20 % by volume of spherical alumina, at least 90 % by weight of which has an average particle size of 3 to 25 μm , and
 - (3) 10 to 1 % by volume of alumina, at least 90 % by weight of which has a particle size of 1 to 7 μm ,
- the percentages by volume adding up to 100 %.

The particle size distribution is determined with a laser scanner (CIS supplied by LOT GmbH, Darmstadt, Germany). This is done by measuring the particles of the defined 90 % by weight range without the two tail ranges of the distribution curve. The percentages by volume relate to the solids present in the powder mixture.

In a preferred embodiment of the formulation of the invention, the mixture comprises

- a) 65 to 75 % by volume of component (1),
 - b) 35 to 22 % by volume of component (2), and
 - c) 7 to 1 % by volume of component (3),
- the percentages by volume adding up to 100 %.

In a further preferred embodiment of the formulation of the invention, the mixture comprises

- a) 70 to 75 % by volume of component (1),
 - b) 30 to 22 % by volume of component (2), and
 - c) 7 to 1 % by volume of component (3),
- the percentages by volume adding up to 100 %.

Irregular shape means particles which have not been subjected to an aftertreatment, for

example the form in which they are obtained after grinding.

The particle diameter of component (1) is preferably 30 to 100 μm , that of component (2) is preferably 3 to 20 μm , and that of component (3) is preferably 1 to 5 μm .

The remaining 10 % by weight of component (1) may contain particles having a diameter larger than 120 μm and up to 200 μm , as well as smaller than 20 μm and up to 0.1 μm . The remaining 10 % of component (2) may contain particles having a diameter larger than 25 μm and up to 40 μm , as well as smaller than 3 μm and up to 0.01 μm . And the remaining 10 % of component (3) may contain particles having a diameter larger than 7 μm and up to 20 μm , and smaller than 1 μm and up to 0.001 μm .

The novel mixtures can be prepared by mixing the three components. Particulate aluminas are known and commercially available. Fractions having defined ranges of particle size are obtainable by conventional separation methods. These separation methods also make it possible to obtain fractions such that the percentage of the tail ranges of the distribution curves is diminished or removed. Thus the three fractions of the novel powder mixture comprise at least 95 % by weight or 100 % by weight of the particles having the particle diameters previously defined. Spherical particles may typically be prepared by sintering or melt processes. The preparation of different modifications of alumina particles is known in the art. Components (2) and (3) can be in the form of different modifications.

The novel mixtures are admirably suited for use as fillers for polymers to enhance thermal conductivity, and the abrasiveness of the formulation is of a low order.

In another of its aspects, the invention relates to a homogeneously blended formulation comprising

- a) 10 to 95 % by weight of a thermoplastic or structurally crosslinked polymer, and
- b) 90 to 5 % by weight of the previously described powder mixture.

The formulation will normally comprise 10 to 90 % by weight of polymer and 90 to 10 % by weight of the powder mixture. Depending on the envisaged end use, the loading of the powder mixture in the polymer can vary in volume. Thus for many moulded parts of which no very high thermal conductivity is expected, a loading of 5 to 50 % by weight, preferably 10 to 40 % by weight, of the powder mixture will meet the requirements of articles of use in respect of thermal conductivity. It is desired to achieve a very high

thermal conductivity, as for encapsulating electrical or electronic components, the loading of powder mixture will normally be more than 50 % by weight, preferably 60 to 90 % by weight and, most preferably, 70 to 90 % by weight,

The thermoplastic polymers may be selected from the following polymers, copolymers or mixtures thereof:

1. Polymers of monoolefins and diolefins, for example polypropylene, polyisobutylene, polybut-1-ene, polymethylpent-1-ene, polyisoprene or polybutadiene, as well as polymers of cycloolefins, for example of cyclopentene or norbornene, polyethylene (which can be uncrosslinked or crosslinked), for example high density polyethylene (HDPE), low density polyethylene (LDPE and linear low density polyethylene (LLDPE).
2. Mixtures of the polymers mentioned under 1), for example mixtures of polypropylene with polyisobutylene, polypropylene with polyethylene (for example PP/HDPE, PP/LDPE) and mixtures of different types of polyethylene (for example LDPE/HDPE).
3. Copolymers of monoolefins and diolefins with each other or with other vinyl monomers, for example ethylene/propylene copolymers linear low density polyethylene (LLDPE) and mixtures thereof with low density polyethylene (LDPE), propylene/but-1-ene copolymers, ethylene/hexene copolymers, ethylene/methylpentene copolymers, ethylene/heptene copolymers, ethylene/octene copolymers, propylene/butadiene copolymers, isobutylene/isoprene copolymers, ethylene/alkyl acrylate copolymers, ethylene/alkyl methacrylate copolymers, ethylene/vinyl acetate or ethylene/acrylic acid copolymers and their salts (ionomers), as well as terpolymers of ethylene with propylene and a diene such as hexadiene, dicyclopentadiene or ethylenenorbornene; and also mixtures of such copolymers with each other and with polymers mentioned in 1) above, for example polypropylene/ethylene propylene copolymers, LDPE/EVA, LDPE/EAA, LLDPE/EVA and LLDPE/EAA.
- 3a. Hydrocarbon resins (for example C₅-C₉), including hydrogenated modifications thereof (for example tackifiers).
4. Polystyrene, poly-(p-methylstyrene), poly-(α -methylstyrene).

5. Copolymers of styrene or α -methylstyrene with dienes or acrylic derivatives, for example styrene/butadiene, styrene/acrylonitrile, styrene/alkylmethacrylate, styrene/butadiene/alkylacrylate, styrene/ maleic anhydride, styrene/acrylonitrile/methyl acrylate; mixtures of high impact strength from styrene copolymers and another polymer, for example from a polyacrylate, a diene polymer or an ethylene/propylene/diene terpolymer; and block copolymers of styrene, for example styrene/butadiene/styrene, styrene/isoprene/styrene, styrene/ethylene/butylene/styrene or styrene/ethylene/propylene/styrene.
6. Graft copolymers of styrene or α -methylstyrene, for example styrene on polybutadiene, styrene on polybutadiene/styrene or polybutadiene/acrylonitrile; styrene and acrylonitrile (or methacrylonitrile) on polybutadiene; styrene and maleic anhydride or maleimide on polybutadiene; styrene, acrylonitrile and maleic anhydride or maleimide on polybutadiene; styrene, acrylonitrile and methyl methacrylate on polybutadiene, styrene and alkyl acrylates or methacrylates on polybutadiene, styrene and acrylonitrile on ethylene/propylene/diene terpolymers, styrene and acrylonitrile on polyalkylacrylates or polyalkylmethacrylates, styrene and acrylonitrile on acrylate/butadiene copolymers, as well as mixtures thereof with the copolymers listed under 5), for example the copolymer mixtures known as ABS, MBS, ASA or AES polymers.
7. Halogenated polymers such as polychloroprene, chlorinated rubbers, chlorinated or sulfochlorinated polyethylene, copolymers of ethylene and chlorinated ethylene, epichlorohydrin homo- and copolymers, preferably polymers of halogenated vinyl compounds, for example poly- vinylchloride, polyvinylidene chloride, polyvinyl fluoride, polyvinylidene fluoride, as well as copolymers thereof, for example vinyl chloride/vinylidene chloride, vinyl chloride/vinyl acetate or vinylidene chloride/vinyl acetate copolymers.
8. Polymers derived from α,β -unsaturated acids and derivatives thereof, such as polyacrylates and polymethacrylates, polyacrylamides and polyacrylonitriles.
9. Copolymers of the monomers mentioned under 8) with each other or with other unsaturated monomers, for example acrylonitrile/butadiene copolymers, acrylonitrile/alkylacrylate copolymers, acrylonitrile/alkoxyalkylacrylate or acrylonitrile/vinyl halide copolymers or acrylonitrile/alkylmethacrylate/butadiene terpolymers.

10. Polymers derived from unsaturated alcohols and amines or the acyl derivatives or acetals thereof, such as polyvinyl alcohol, polyvinyl acetate, polyvinyl stearate, polyvinyl benzoate, polyvinyl maleate, polyvinylbutyrate, polyallyl phthalate or polyallylmelamine; as well as their copolymers with the olefins mentioned in 1) above.
11. Homopolymers and copolymers of cyclic ethers such as polyalkylene glycols, polyethylene oxide, polypropylene oxide or copolymers thereof with bisglycidyl ethers.
12. Polyacetals such as polyoxymethylene and those polyoxymethylenes which contain ethylene oxide as a comonomer; polyacetals modified with thermoplastic polyurethanes, acrylates or MBS.
13. Polyphenylene oxides and sulfides and mixtures thereof with polystyrene or polyamides.
14. Polyurethanes which are derived from polyethers, polyesters or polybutadienes carrying terminal hydroxyl groups on the one hand and aliphatic or aromatic polyisocyanates on the other, as well as precursors thereof.
15. Polyamides and copolyamides which are derived from diamines and dicarboxylic acids and/or from aminocarboxylic acids or the corresponding lactams, such as polyamide 4, polyamide 6, polyamide 6/6, 6/10, 6/9, 6/12 and 4/6, polyamide 11, polyamide 12, aromatic polyamides obtained by condensation of m-xylene, diamine and adipic acid; polyamides prepared from hexamethylenediamine and isophthalic and/or terephthalic acid, with or without an elastomer as modifier, for example poly-2,4,4-trimethylhexamethylene terephthalamide or poly-m-phenylene isophthalamide; block copolymers of the aforementioned polyamides with polyolefins, olefin copolymers, ionomers or chemically bonded or grafted elastomers; or with polyethers, for example with polyethylene glycol, polypropylene glycol or polytetramethylene glycol; and also polyamides or copolyamides modified with EPDM or ABS, and polyamides condensed during processing (RIM polyamide systems).
16. Polyureas, polyimides and polyamide-imides and polybenzimidazoles.
17. Polyesters derived from dicarboxylic acids and diols and/or from hydroxycarboxylic acids or the corresponding lactones, such as poly-ethylene terephthalate, polybutylene

terephthalate, poly-1,4-dimethylolcyclohexane terephthalate, polyhydroxybenzoates as well as block-copolyether esters derived from hydroxyl-terminated polyethers; and also polyesters modified with polycarbonates or MBS.

18. Polycarbonates and polyester carbonates.

19. Polysulfones, polyether sulfones and polyether ketones.

20. Polyethers of diglycidyl compounds, including diglycidyl ethers and diols, for example of bisphenol A diglycidyl ether and bisphenol A.

21. Natural polymers such as cellulose, rubber, gelatine and chemically modified homologous derivatives thereof such as cellulose acetates, cellulose propionates and cellulose butyrates, or the cellulose ethers, such as methylcellulose; as well as rosins and their derivatives.

22. Mixtures (polyblends) of the aforementioned polymers, for example PP/EPDM, Polyamide 6/EPDM or ABS, PVC/EVA, PVS/ABS, PVC/MBS, PC/ABS, PBTP/ABS, PC/ASA, PC/PBT, PVC/CPE, PVC/acrylates, POM/thermoplastic PUR, PC/thermoplastic PUR, POM/acrylate, POM/MBS, PPE/HIPS, PPE/PA 6.6 and copolymers, PA/HDPE, PA/PP, PA/PPO.

The structurally crosslinked polymers may be typically the following polymers:

1. Crosslinked polymers which are derived from aldehydes on the one hand and phenols, ureas and melamines on the other hand, such as phenol/formaldehyde resins, urea/formaldehyde resins and melamine/formaldehyde resins.

2. Drying and non-drying alkyd resins.

3. Unsaturated polyester resins which are derived from copolyesters of saturated and unsaturated dicarboxylic acids with polyhydric alcohols and vinyl compounds as crosslinking agents, and also halogen-containing modifications thereof of low flammability.

4. Crosslinkable acrylic resins derived from substituted acrylic esters such as epoxy acrylates, urethane acrylates or polyester acrylates.
5. Alkyd resins, polyester resins or acrylate resins which are cross-linked with melamine resins, urea resins, polyisocyanates or epoxy resins.
6. Rubber derived from crosslinked polydienes, for example butadiene or isoprene; silicon rubber.
7. Crosslinked epoxy resins which are derived from polyepoxides, for example from bisglycidyl ethers or from cycloaliphatic diepoxides.

Among the crosslinked polymers, crosslinked epoxy resins are preferred which, as polyepoxides, are derived preferably from glycidyl compounds which contain on average two epoxy groups in the molecule. Particularly suitable glycidyl compounds are those which contain two glycidyl groups, β -methylglycidyl groups or 2,3-epoxycyclopentyl groups attached to a hetero atom (e.g. sulfur, preferably oxygen or nitrogen), in particular bis(2,3-epoxycyclopentyl) ether; diglycidyl ethers of polyhydric aliphatic alcohols, such as 1,4-butanediol, or polyalkylene glycols, such as polypropylene glycols; diglycidyl ethers of cycloaliphatic polyols, such as 2,2-bis(4-hydroxycyclohexyl)propane; diglycidyl ethers of polyhydric phenols, such as resorcinol, bis(p-hydroxyphenyl)methane, 2,2-bis-(p-hydroxyphenyl)propane (= diomethane), 2,2-bis(4'-hydroxy-3',5'-dibromophenyl)propane, 1,3-bis(p-hydroxyphenyl)ethane; bis(β -methylglycidyl) ethers of the above dihydric alcohols or dihydric phenols; diglycidyl esters of dicarboxylic acids, such as phthalic acid, terephthalic acid, Δ_4 -tetrahydrophthalic acid and hexahydrophthalic acid; N,N-diglycidyl derivatives of primary amines and amides and heterocyclic nitrogen bases which contain two N-atoms, and N,N'-diglycidyl derivatives of disecundary diamides and diamines, such as N,N-diglycidylaniline, N,N-diglycidyltoluidine, N,N-diglycidyl-p-aminophenyl methyl ether, N,N'-dimethyl-N,N'-diglycidylbis(p-aminophenyl)methane; N',N''-diglycidyl-N-phenyl-isocyanurate; N,N'-diglycidyl ethyleneurea; N,N'-diglycidyl-5,5-dimethylhydantoin, N,N'-diglycidyl-5-isopropyl-hydantoin, N,N-methylenebis-(N',N'-diglycidyl-5,5-dimethylhydantoin), 1,3-bis(N-glycidyl-5,5-dimethylhydantoin)-2-hydroxypropane; N,N'-diglycidyl-5,5-dimethyl-6-isopropyl-5,6-dihydrouracil, tri-glycidyl isocyanurate.

A preferred group of epoxy resins comprises glycidylated novolaks, hydantoins,

aminophenols, bisphenols and aromatic diamines or cycloaliphatic epoxy compounds. Particularly preferred epoxy resins are glycidylated cresol novolaks, bisphenol A and bisphenol F diglycidyl ether, hydantoin-N,N'-bisglycide, p-aminophenol triglycide, diaminodiphenylmethane tetraglycide, vinylcyclohexene dioxide, 3,4-epoxycyclohexyl-methyl-3,4-epoxycyclohexanecarboxylate or mixtures thereof.

Further suitable epoxy resins are prereacted adducts of such epoxy compounds with epoxy hardeners, for example an adduct of bisphenol A diglycidyl ether and bisphenol A, or adducts which have been prereacted with oligoesters which carry two terminal carboxyl groups and epoxides.

Suitable hardeners for epoxy resins are acid or basic compounds. Illustrative examples of suitable hardeners are: amines, including aliphatic, cycloaliphatic or aromatic, primary, secondary and tertiary amines, ethylenediamine, hexamethylenediamine, trimethylhexamethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, N,N-dimethylpropylene-1,3-diamine, N,N-diethylpropylene-1,3-diamine, 2,2-bis-(4'-aminocyclohexyl)propane, 3,3,5-trimethyl-3-(aminomethyl)cyclohexylamine (isophoronediamine), Mannich bases such as 2,4,6-tris(dimethylaminomethyl)phenol, m-phenylenediamine, p-phenylenediamine, bis(4-aminophenyl)methane, bis(4-amino-phenyl)sulfone, xylylenediamine; aminoalcohols, such as aminoethanol, 1,3-amino-propanol, diethanolamine or triethanolamine; adducts of acrylonitrile with polyalkylenepolyamines or monoepoxides (ethylenic oxide, propylene oxide) with polyalkylene-polyamines (diethylenetriamine, triethylenetetramine); adducts of an excess of polyamines (diethylenetriamine, triethylenetetramine) and polyepoxides such as bisphenol A diglycidyl ethers; polyamides, preferably those from aliphatic polyamines (diethylene-triamine, triethylenetetramine) and di- or trimerised unsaturated fatty acids (dimerised linseed oil fatty acid, Versamid[®]); dicyandiamide; polysulfides (Thiokol[®]); aniline-formaldehydes; polyhydric phenols (resorcinol, 2,2-bis(4-hydroxyphenyl)propane) or phenol-formaldehyde resins; polybasic carboxylic acids and the anhydrides thereof, such as phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, 4-methyl-hexahydrophthalic anhydride, 3,6-endomethylene-tetrahydrophthalic anhydride, 4-methyl-3,6-endomethylen-tetrahydrophthalic anhydride (methyladipic anhydride), 3,4,5,6,7,7-hexachloroendomethylene-tetrahydrophthalic anhydride, succinic anhydride, adipic anhydride, trimethyladipic anhydride, sebacic anhydride, maleic anhydride, dodecylsuccinic anhydride, pyromellitic dianhydride, trimellitic anhydride, benzo-phenonetetracarboxylic dianhydride, or mixtures of such anhydrides.

A preferred group of hardeners comprises polyamines, novolaks, polyaminoamides and polycarboxylic anhydrides.

The epoxy resins can also be additionally cured with curing accelerators or only with thermal curing catalysts. Exemplary of curing accelerators and catalysts are tertiary amines, salts thereof or quaternary ammonium compounds (2,4,6-tris(dimethylamino-methyl)phenol, benzyl dimethylamine, 2-ethyl-4-methylimidazole, triamylammonium phenolate); mono- or polyphenols (phenol, diomethane, salicylic acid); boron trifluoride and the complexes thereof with organic compounds, such as boron trifluoride ether complexes and boron trifluoride amine complexes (BF_3 /monoethylamine complex); phosphoric acid and triphenylphosphite.

Curing accelerators and catalysts are normally added in an amount of 0.1 to 10 % by weight, based on the epoxy resin. Hardeners for epoxy resins are normally used in equimolar amounts, based on the epoxy groups and functional groups of a hardener.

Further additives for enhancing processing properties, the mechanical, electrical and thermal properties, surface properties and light stability can be blended into the novel formulation. Exemplary of such additives are finely particulate fillers, reinforcing fillers, plasticisers, lubricants and mould release agents, adhesion promoters, antioxidants, heat and light stabilisers, pigments and dyes. The maximum amount of additional fillers and/or reinforcing fillers concurrently used is conveniently, together with the novel powder mixture, not more than 95 % by weight, preferably not more than 90 % by weight, based on the formulation.

The novel formulation can be prepared by methods known in plastics technology, conveniently by blending the finely particulate thermally conductive filler with the plastics material before, during or after its production, by plasticising the plastics material and blending it with the filler by calendering, extrusion or injection moulding to prepare granulates or mouldings. It is also possible to make a dry blend of the powdered plastics material with the filler or to suspend the filler in a solution of the plastics material and then to remove the solvent.

When using thermoset resins and structurally crosslinked polymers, the finely particulate filler is conveniently added prior to shaping and to curing or crosslinking, typically by

jointly blending the resin components with the filler, which may be incorporated beforehand in one component.

The powder mixture can be blended into the plastics material in the form of the mixture itself, in a combination of two components, followed by addition of the third component, or by the addition of the individual components in succession.

The novel mixture is especially suitable for the production of epoxy casting resins having a high-volume loading of filler such that moulded articles prepared therefrom have thermal conductivities at fairly low temperature of more than 3.2 and even more than 4 W/mK. Despite the high-volume loading, the viscosity of the casting resins is still so low that they are in some cases pourable when subjected to heat and/or vibration and can be readily processed to moulded articles.

The invention further relates to an epoxy casting resin formulation which comprises 70 to 90 % by weight, preferably 75 to 90 % by weight and, most preferably, 80 to 90 % by weight, of the novel powder mixture of aluminas.

Suitable epoxy resins are those previously mentioned above. Preferred epoxy resins are those based on bisphenol diglycidyl ethers or advanced bisphenol diglycidyl ethers, typically bisphenol A and bisphenol F diglycidyl ether, and a polycarboxylic anhydride, such as phthalic anhydride or hydrophthalic anhydride, as hardener, which epoxy resins are preferably cured in the presence of a hardening accelerator such as N-methylimidazole.

The novel formulation is a useful moulding material for the production of thermally conductive moulded articles of all kinds, including films, sheets, ribbons, fibres, boards, semi-finished products, shaped articles and casings. The conventional techniques of plastics processing can be used, typically casting, calendering, injection moulding, extruding, deep drawing, compression moulding and sintering. The novel formulation is especially suitable for the production of heating elements, resin adhesives and hot melt adhesives, preferably for bonding metals, and also as thermally conductive sealing material especially for electrical and electronic components.

The invention further relates to the use of the novel formulation or of the casting resin formulation for the production of thermally conductive moulded articles and composites.

In yet another of its aspects, the invention relates to the use of the casting resin formulation as resin adhesive for bonding metals or as sealing material for electrical and electronic components.

The following Examples illustrate the invention in more detail. The thermal conductivity is measured by the thermal comparison method using Pyroceram[®] 9606 as reference material. The method is described by L. C. Hulstrom et al. in "Round-Robin Testing Of Thermal Conductivity Reference Materials", Proceedings of Thermal Conductivity 19, October 20-23, 1985, Cookevelli, Tennessee, edited by D.W. Yarbrough.

Example 1: The following alumina fractions are chosen to prepare a casting resin formulation:

1. Sintered, spherical α - Al_2O_3 , median diameter 47 μm , particle diameter of the defined 90 % by weight range from 30 to 100 μm .
2. Commercial spherical α - and δ - Al_2O_3 (Alunabeads CBA-10[®], Showa Denko, Japan), median diameter 9 μm , particle diameter of the defined 90 % by weight range from 3 to 20 μm .
3. Commercial Al_2O_3 (CTB 5/6FG[®], Alcoa), median diameter 3.5 μm , particle diameter of the defined 90 % by weight range from 1 to 5 μm

71 % by weight (70 % by volume) of component 1 and 28 % by weight (29 % by volume) component 2 are stirred for 7 hours in a polypropylene bottle (stirrer with mobile blades). Afterwards 1 % by weight (1 % by volume) of component 3 are added and stirring is continued for 1 hour. With stirring, the powder mixture is homogeneously blended at 80°C into an epoxy casting resin comprising 50.9 % by weight of bisphenol F diglycidyl ether, 48.9 % by weight of hexahydrophthalic anhydride and 0.2 % by weight of N-methylimidazole. The amount is chosen such that the formulation is still pourable under vibration. The formulation is poured into an aluminium mould and then cured for 4 hours at 80°C and for 18 hours at 120°C. The loading of the powder mixture is determined from the density and is 73 % by volume (84 % by weight). The thermal conductivity of the cured specimen at 40°C is 4.05 W/mK.

Example 2: In accordance with the procedure described in Example 1, an epoxy casting resin containing 88 % by weight (70.2 % by volume) of the following filler formulation is prepared:

72.9 % by weight (70.2 % by volume) of component 1 according to Example 1;
23.1 % by weight (24 % by volume) of component 2 according to Example 1;
4 % by weight (4 % by volume) of component 3 according to Example 1.
The thermal conductivity is 3.6 W/mK.

Example 3: In accordance with the procedure described in Example 1, an epoxy casting resin containing 87.6 % by weight (69.3 % by volume) of the following filler formulation is prepared:

73.8 % by weight (73 % by volume) of component 1 according to Example 1;
22.2 % by weight (23 % by volume) of component 2 according to Example 1;
4 % by weight (4 % by volume) of component 3 according to Example 1.
The thermal conductivity is 3.3 W/mK.

Example 4: In accordance with the procedure described in Example 1, an epoxy casting resin containing 88.4 % by weight (70.9 % by volume) of the following filler formulation is prepared:

59 % by weight (58 % by volume) of component 1 according to Example 1;
35 % by weight (34 % by volume) of component 2 according to Example 1;
7 % by weight (4 % by volume) of component 3 according to Example 1.
The thermal conductivity is 3.8 W/mK.

What is claimed is:

1. A powder mixture of alumina with fractions of different particle size and external shape, which mixture comprises:
 - (1) 55 to 75 % by volume of spherical α -alumina, at least 90 % by weight of which has an average particle size of 20 to 120 μm ,
 - (2) 35 to 20 % by volume of spherical alumina, at least 90 % by weight of which has an average particle size of 3 to 25 μm , and
 - (3) 10 to 1 % by volume of alumina, at least 90 % by weight of which has a particle size of 1 to 7 μm ,the percentages by volume adding up to 100 %.
2. A mixture according to claim 1 which comprises
 - a) 65 to 75 % by volume of component (1),
 - b) 35 to 22 % by volume of component (2), and
 - c) 7 to 1 % by volume of component (3),the percentages by volume adding up to 100 %.
3. A mixture according to claim 1 which comprises
 - a) 70 to 75 % by volume of component (1),
 - b) 30 to 22 % by volume of component (2), and
 - c) 7 to 1 % by volume of component (3),the percentages by volume adding up to 100 %.
4. A mixture according to claim 1, wherein the particle diameter of component (1) is in the range from 30 to 100 μm , that of component (2) is from 3 to 20 μm , and that of component (3) is from 1 to 5 μm .
5. A homogeneously blended formulation comprising
 - a) 10 to 95 % by weight of a thermoplastic or structurally crosslinked polymer, and
 - b) 90 to 5 % by weight of the powder mixture as claimed in claim 1.
6. A formulation according to claim 5, which comprises 10 to 90 % by weight of polymer and 90 to 10 % by weight of the powder mixture.

7. A formulation according to claim 5, wherein the structurally crosslinked polymer is an epoxy resin.
8. A casting resin formulation based on epoxy resins, which comprises 70 to 90 % by weight of the powder mixture as claimed in claim 1, based on said formulation.
9. A casting resin formulation according to claim 8, which comprises 75 to 90 % by weight of the powder mixture.
10. A casting resin formulation according to claim 8, which comprises 80 to 90 % by weight of the powder mixture.
11. A casting resin formulation according to claim 8, which comprises a mixture of bisphenol diglycidyl ethers and a polycarboxylic anhydride as hardener.
12. A casting resin formulation according to claim 11, which additionally comprises a curing accelerator.
13. A casting resin formulation according to claim 11, which comprises a bisphenol A or bisphenol F diglycidyl ether.
14. Use of a formulation as claimed in claim 5 for the production of thermally conductive moulded articles and composites.
15. Use of a casting resin formulation as claimed in claim 8 for the production of thermally conductive moulded articles.
16. Use of a casting resin formulation as claimed in claim 8 as resin adhesive for bonding metals or as sealing material for electrical and electronic components.

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